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Title: Fuel Processing for Fuel Cells: Effects on Catalyst Durability and Carbon Formation

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Fuel Processing for Fuel Cells:Effects on Catalyst Durability and Carbon Formation

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Los Alamos National Laboratory

ESA-EPE Fuel Cell Team

Fuel Processing Technical Objectives

Objectives

- Quantify fuel effects on fuel processor performance.
- Quantify fuel and fuel impurity effects on catalyst durability.
- Understand parameters that affect fuel processor lifetime and durability.

Approach

- Examine Fuel Effects on Fuel Processing
  - Examine individual fuel components / component blends / gasoline
  - Carbon formation
  - Gas phase vs. catalytic oxidation
  - Catalyst performance and degradation
- Modeling of fuels
  - Carbon formation modeling
  - Equilibrium modeling
  - Thermodynamic property modeling

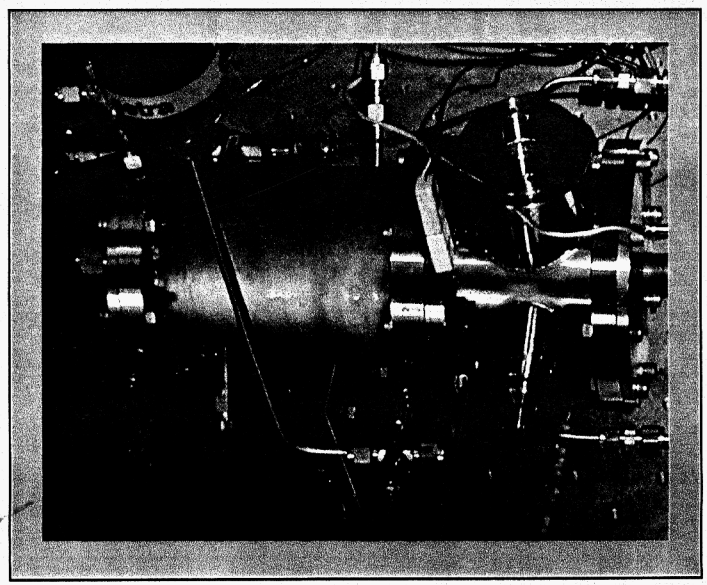
Testing Facilities

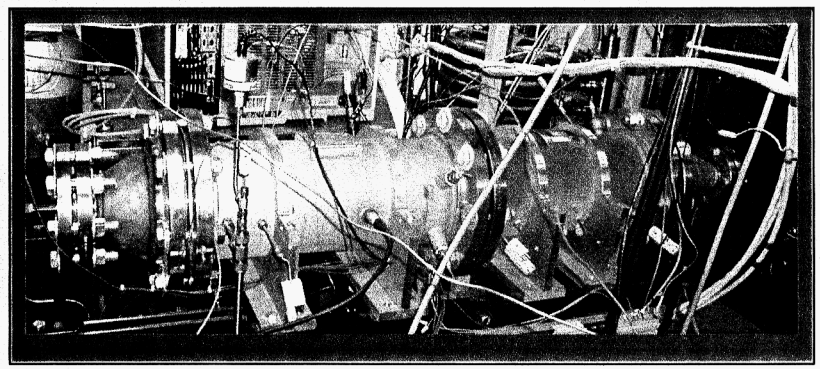
LANL Catalytic

Partial Oxidation/Steam Reforming

Test supported non-proprietary catalysts

Shown with observation windows





Homogeneous partial oxidation

Fuel components testing with homogeneous partial oxidation / catalytic steam reforming

(provided by Nuvera)

Why Homogeneous:

Target of < 30 sec start-up time

Catalyst Degradation Mechanisms

Carbon (Soot) Formation

$2CO \Leftrightarrow C + CO_2$ (Boudart Reaction)

$CH_4 \Leftrightarrow C + 2H_2$ (CH_4 Decomposition)

$CH_4 \rightarrow C_2H_6 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \rightarrow$ aromatics $+ H_2 \rightarrow$ soot

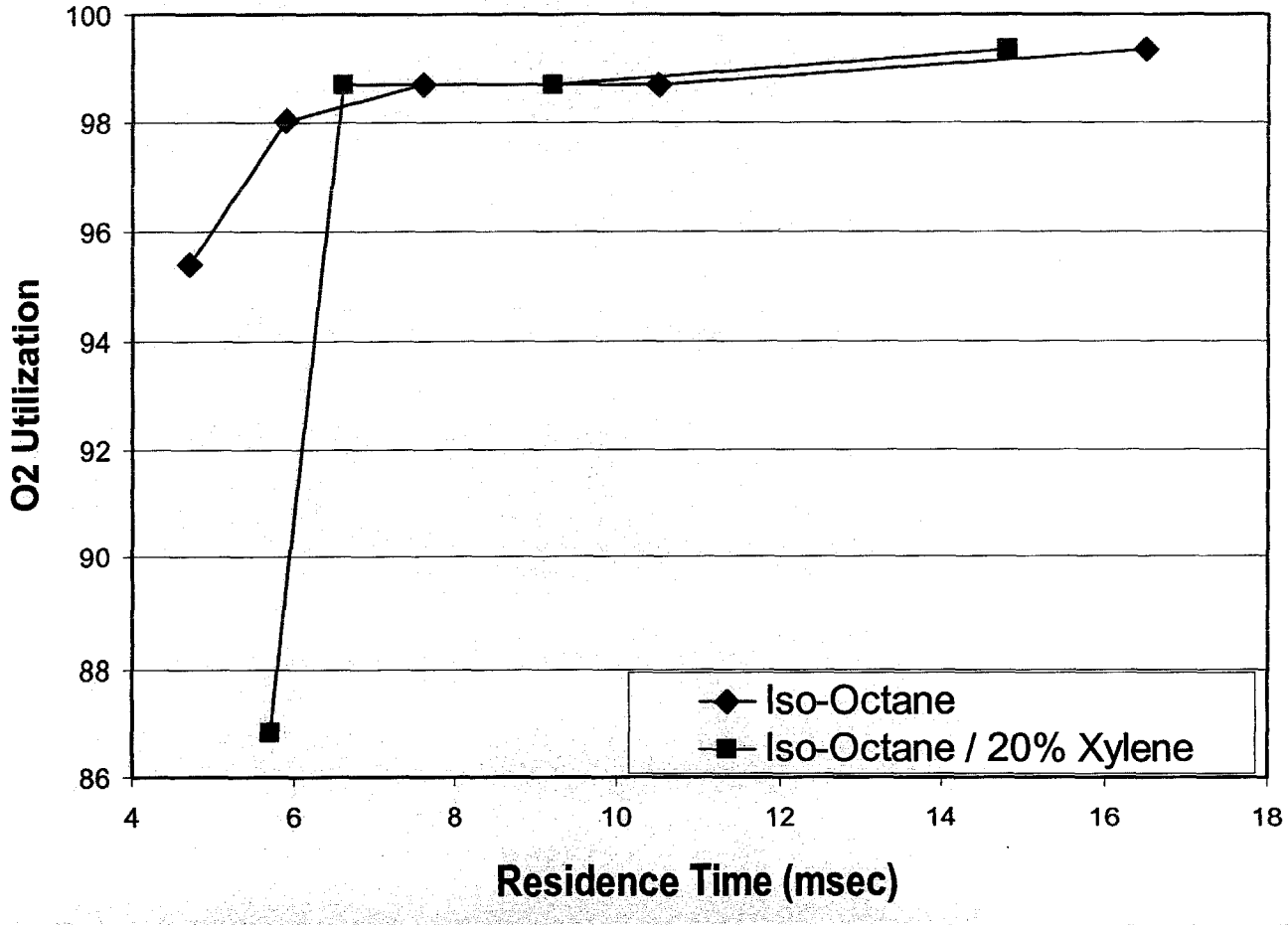
$C_nH_{2n} \rightarrow C_n + nH_2$

- Formation of heavier hydrocarbons such as polycyclic aromatic compounds from aromatics
- Structural change of catalyst particle (sintering, ...)
- Fuel impurities change catalyst activity (poison)

- Methods to help delineate catalyst degradation:
  - Monitor catalyst activity and performance
  - Measure carbon formation
  - Analyze catalyst particles for changes in surface area, elemental composition

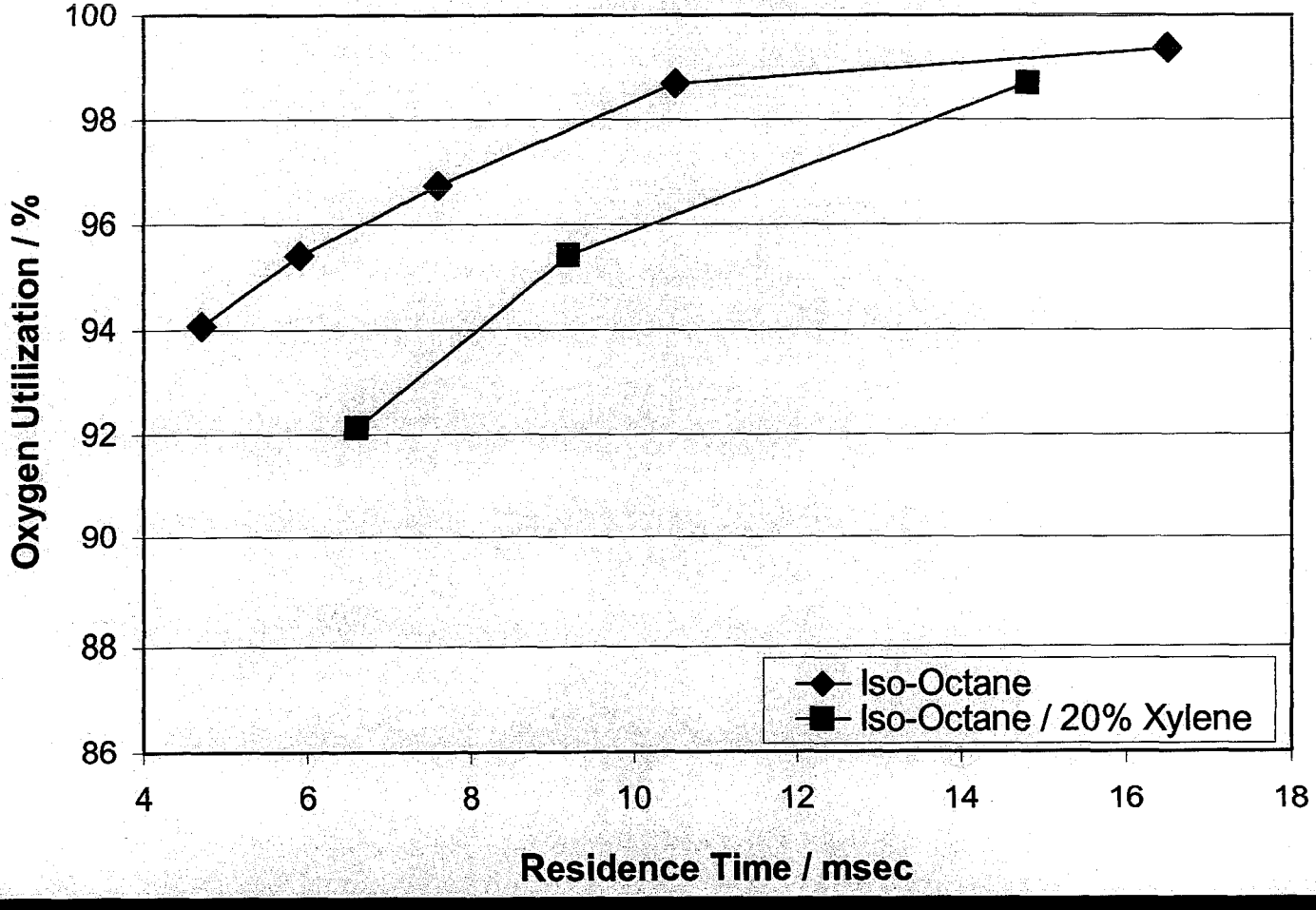
Fuel Effects on O_2 Utilization in Catalytic POx Reactor

Oxidation differences with Iso-Octane and Iso-Octane/20% Xylene
Pt washcoated monolith; (O/C = 1, S/C = 1)



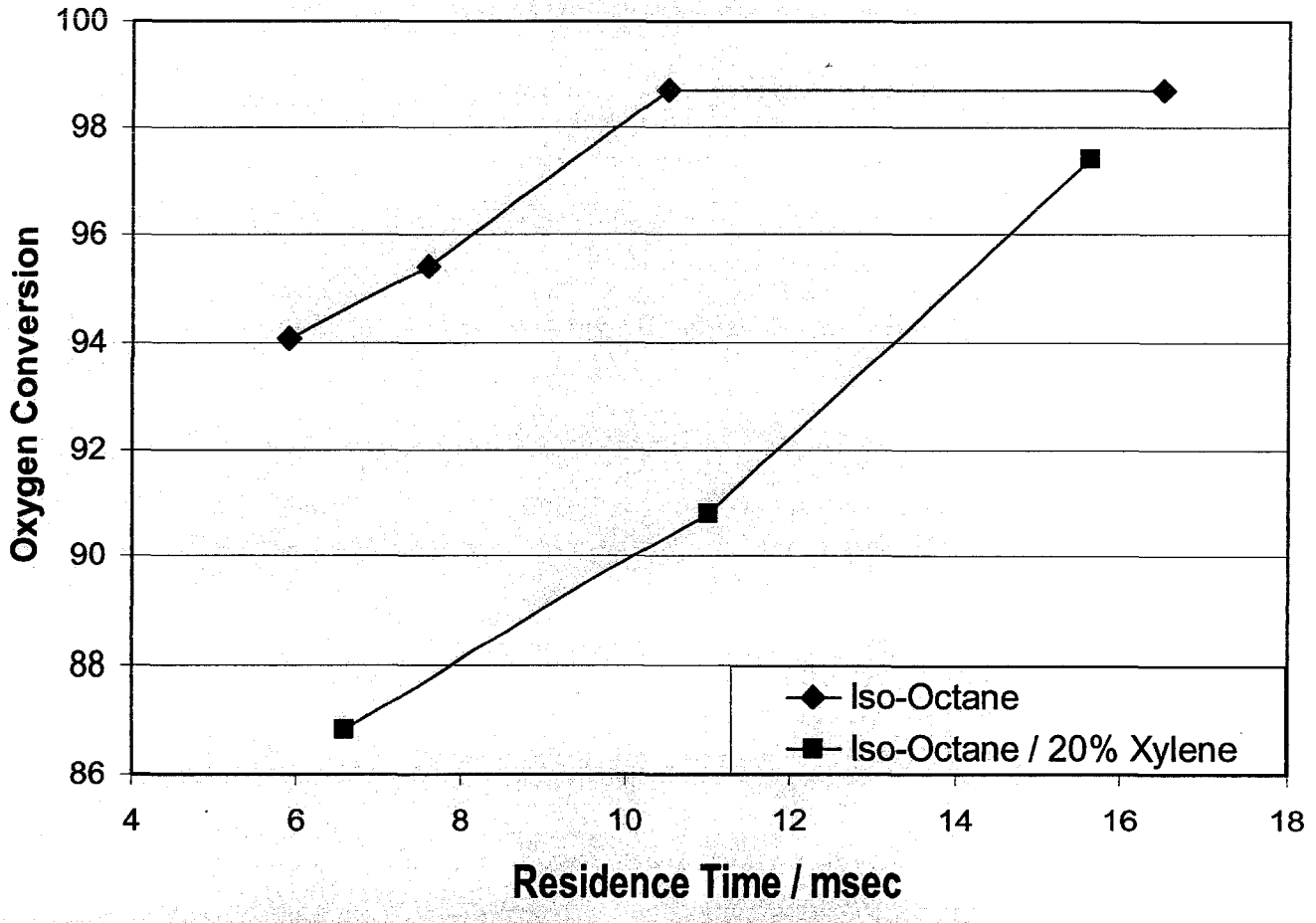
Fuel Effects on O_2 Utilization in Catalytic POx Reactor

Oxidation differences with Iso-Octane and Iso-Octane/20% Xylene
Pt washcoated monolith; (O/C = 0.8, S/C = 1)

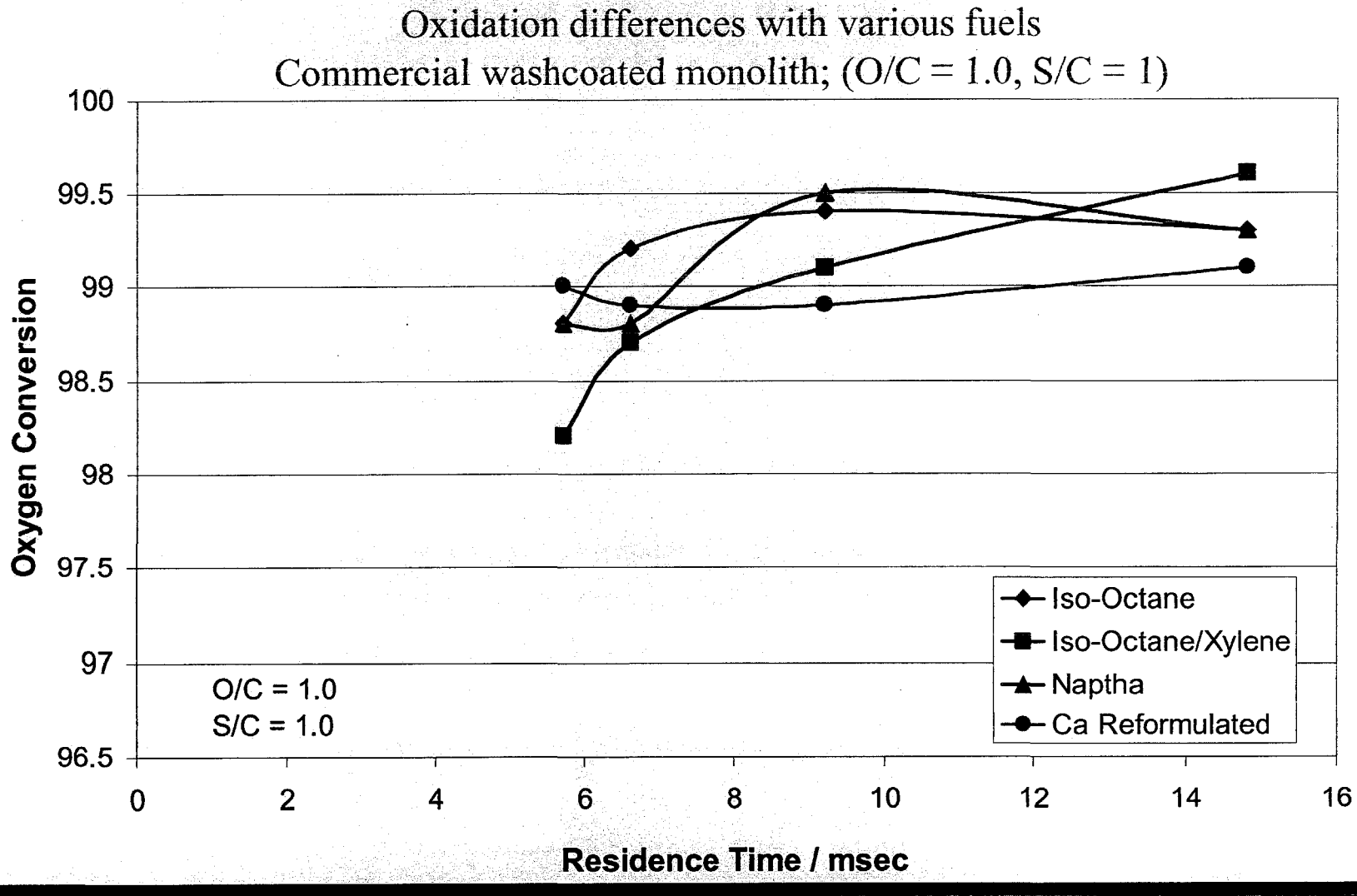


Pt Catalyst in Catalytic POx Reactor

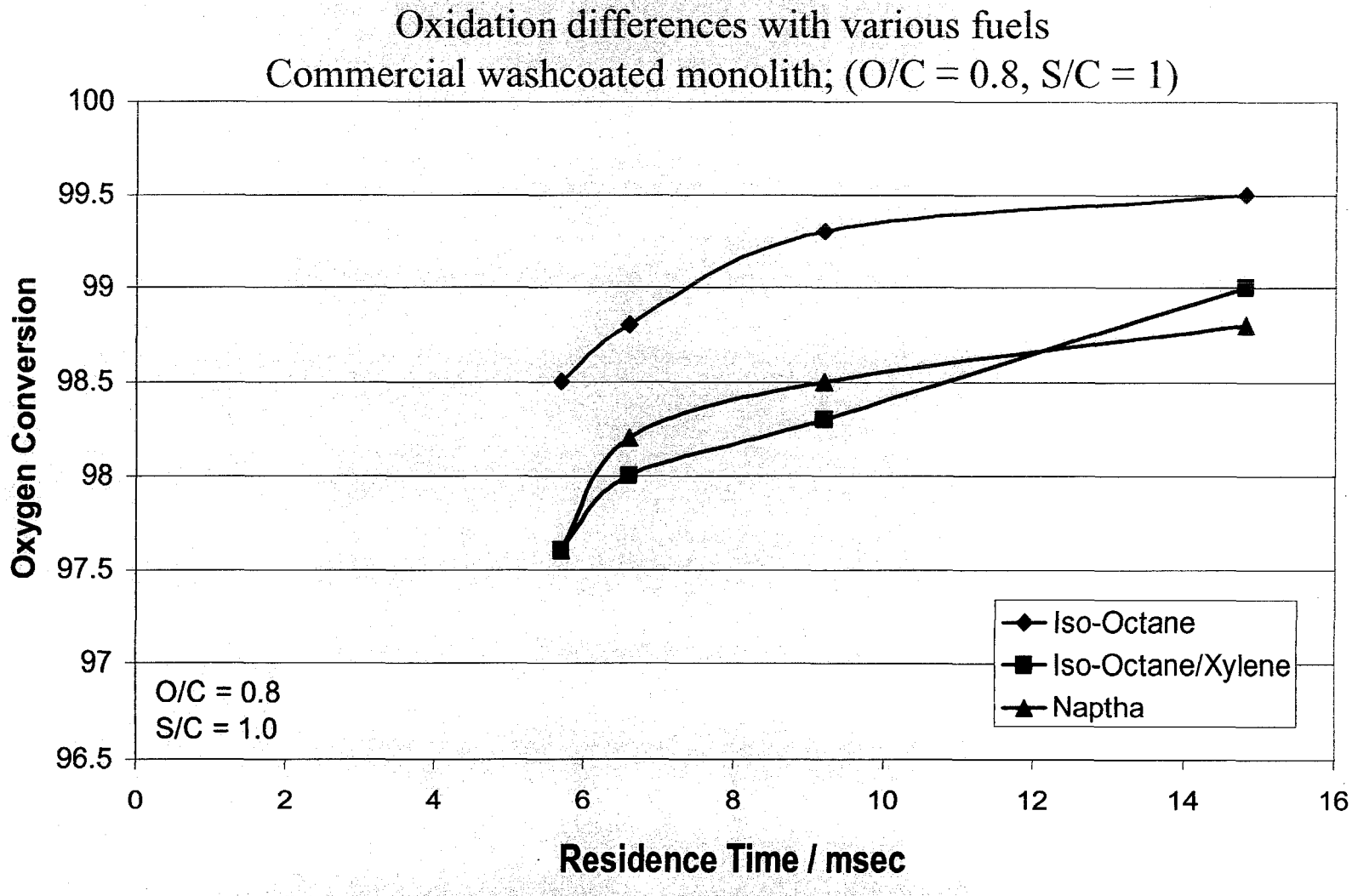
Oxidation differences with Iso-Octane and Iso-Octane/20% Xylene
Pt washcoated monolith; (O/C = 0.7, S/C = 1)



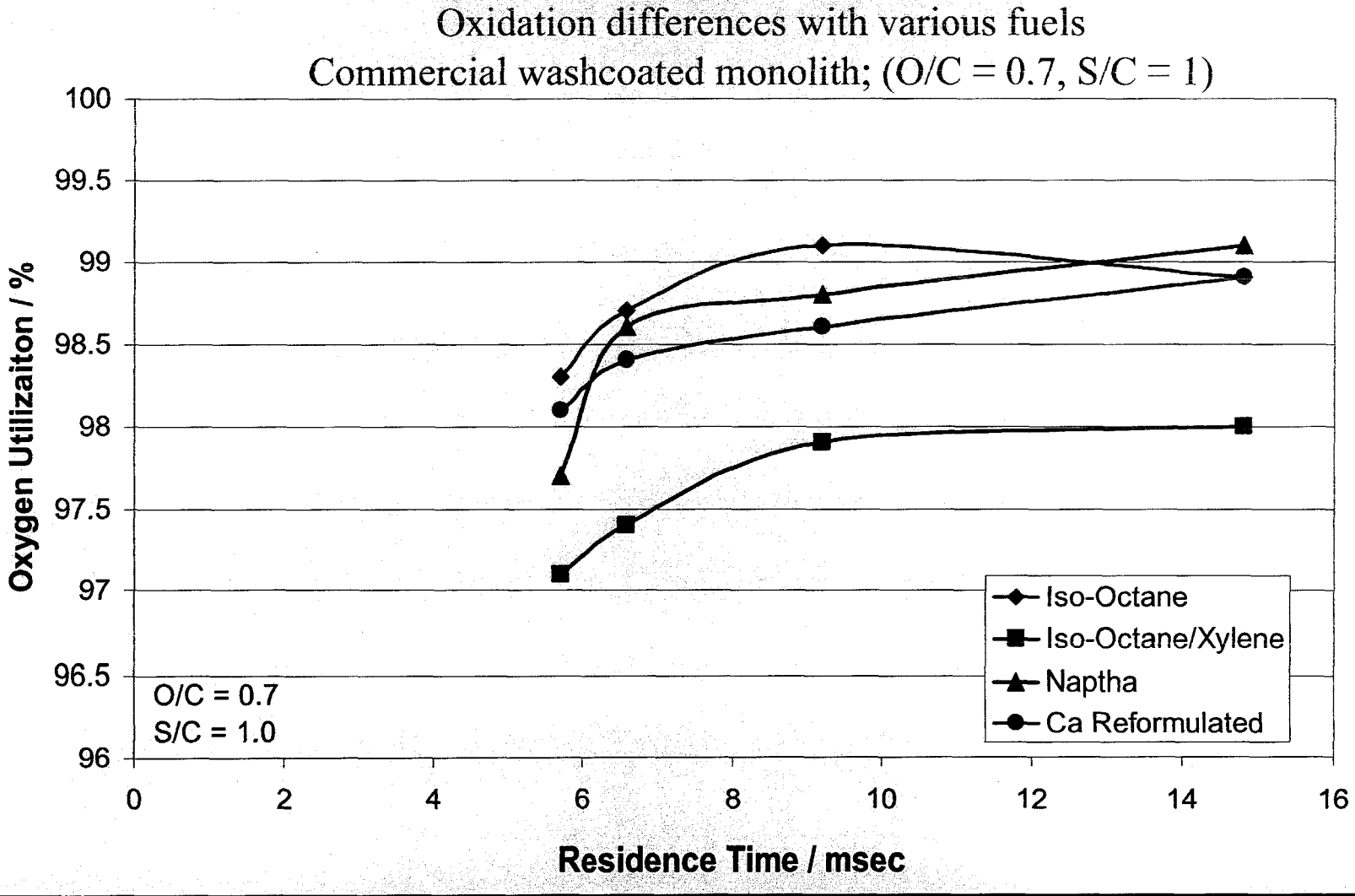
Fuel Effects on O_2 Utilization in Catalytic POx Reactor



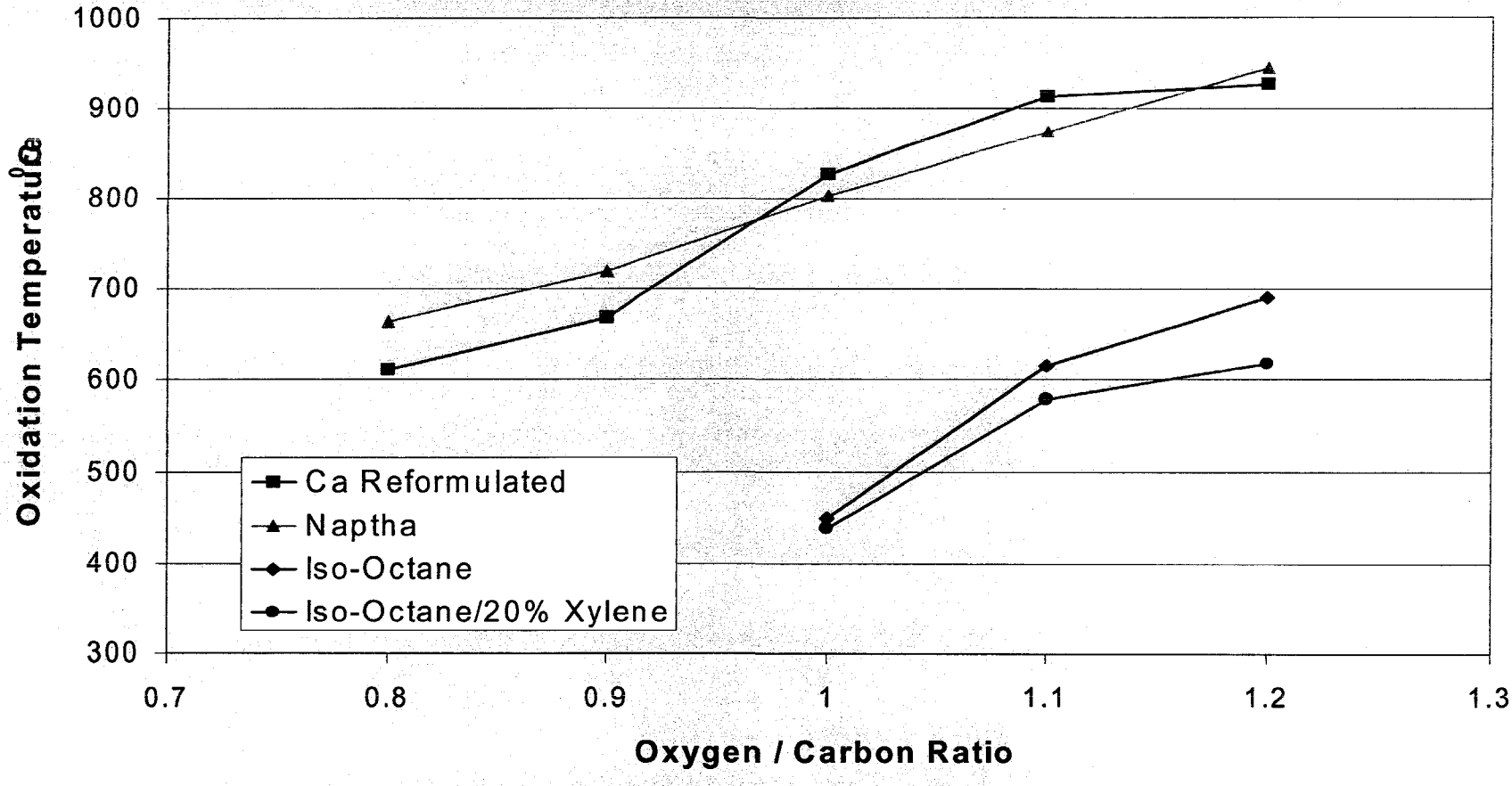
Fuel Effects on O_2 Utilization in Catalytic POx Reactor



Fuel Effects on O_2 Utilization in Catalytic POx Reactor



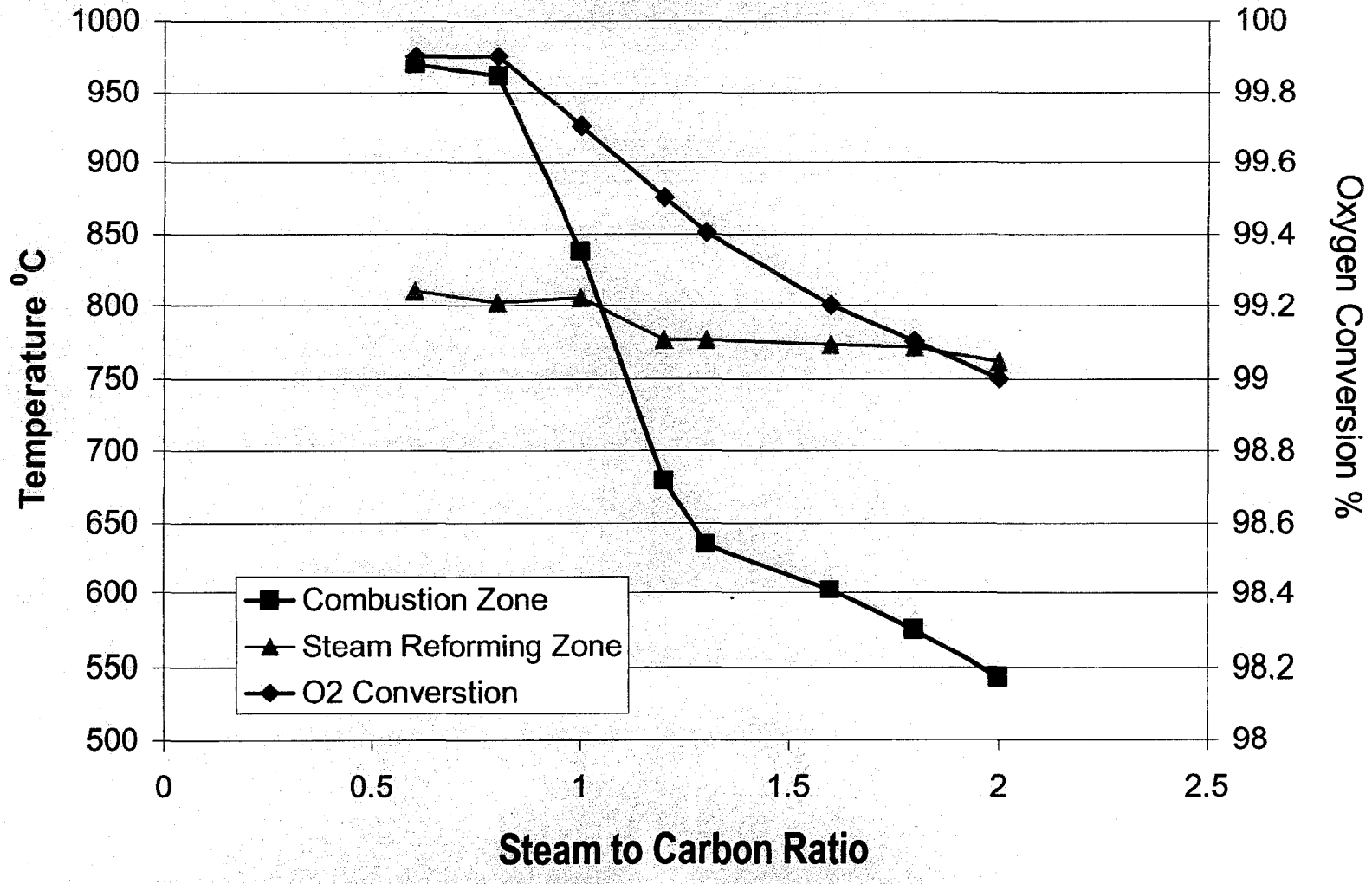
Fuels During Homogeneous Oxidation



Homogeneous oxidation was easier with 'real' fuels

Difficult to keep combustion with pure components iso-octane and iso-octane/xylene

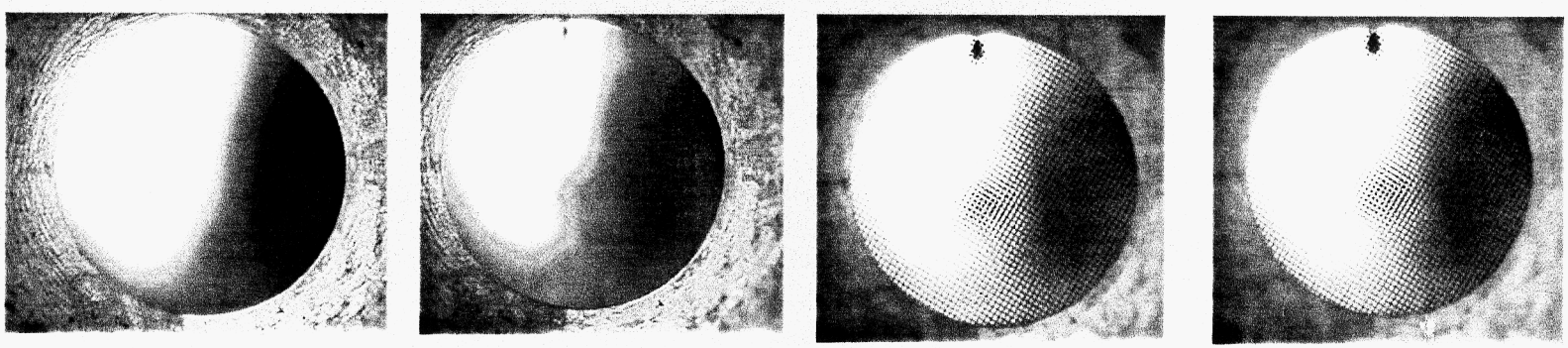
S/C Effect on Homogeneous Naptha Oxidation



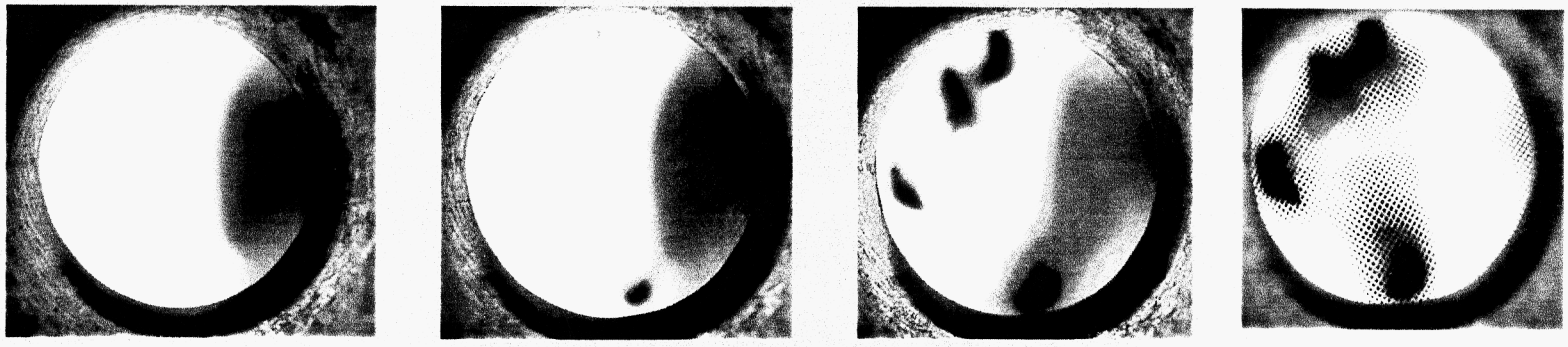
Outlet Images of POx Monolith

Iso-Octane

O/C = 1.14 | O/C = 0.97 | O/C = 0.85 | O/C = 0.76



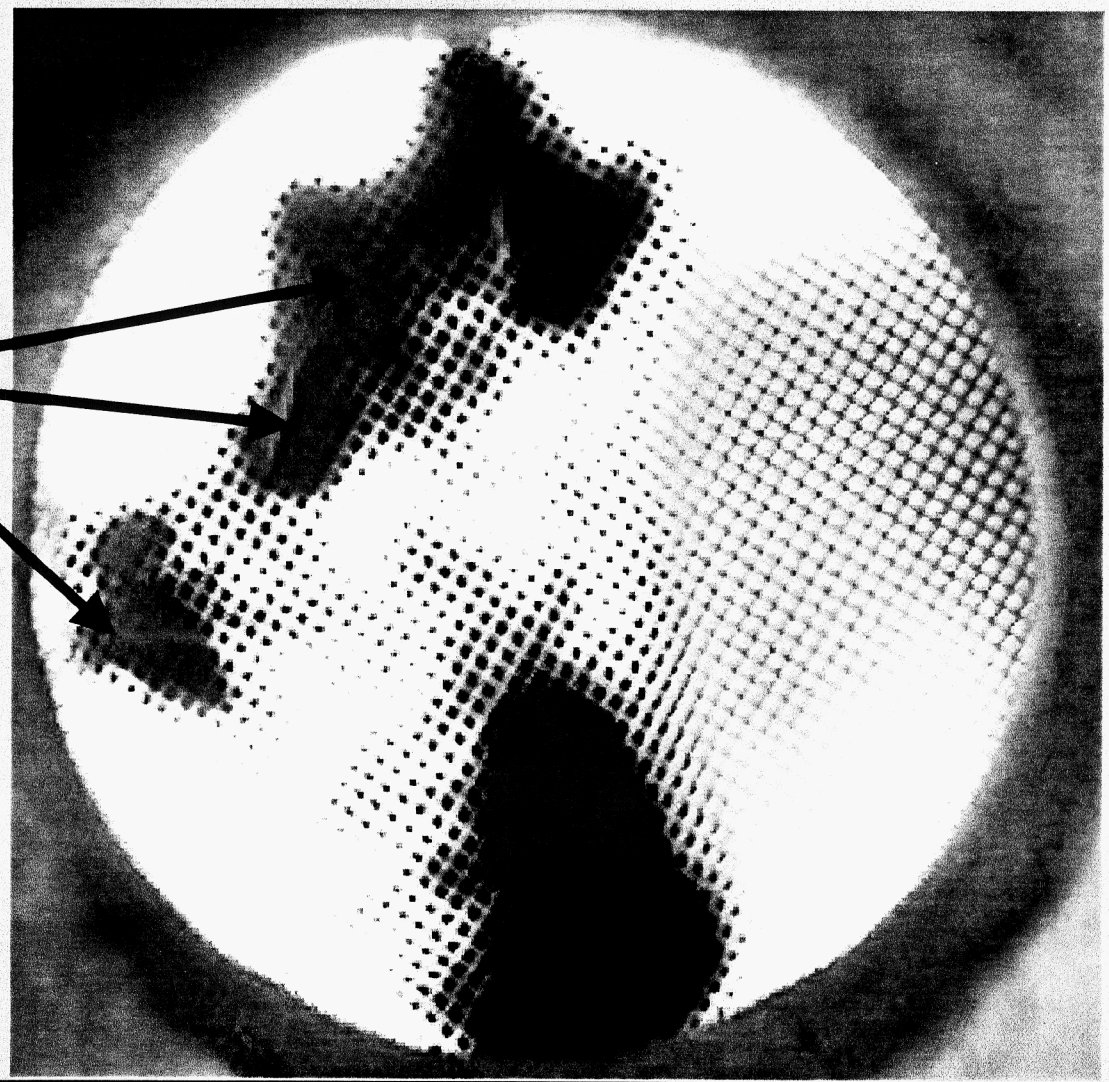
Philips Naptha



S/C = 1.0, Residence time = 15 msec

Carbon Formation

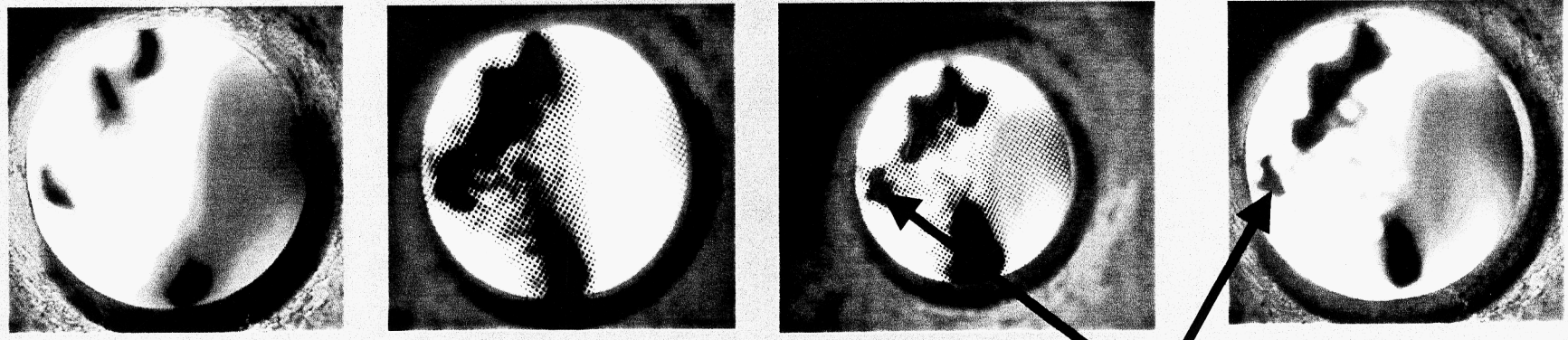
Carbon Formation Visible



Carbon Formation

Partial Oxidation of Philips Naptha Stream

Decreasing O/C → Increasing O/C



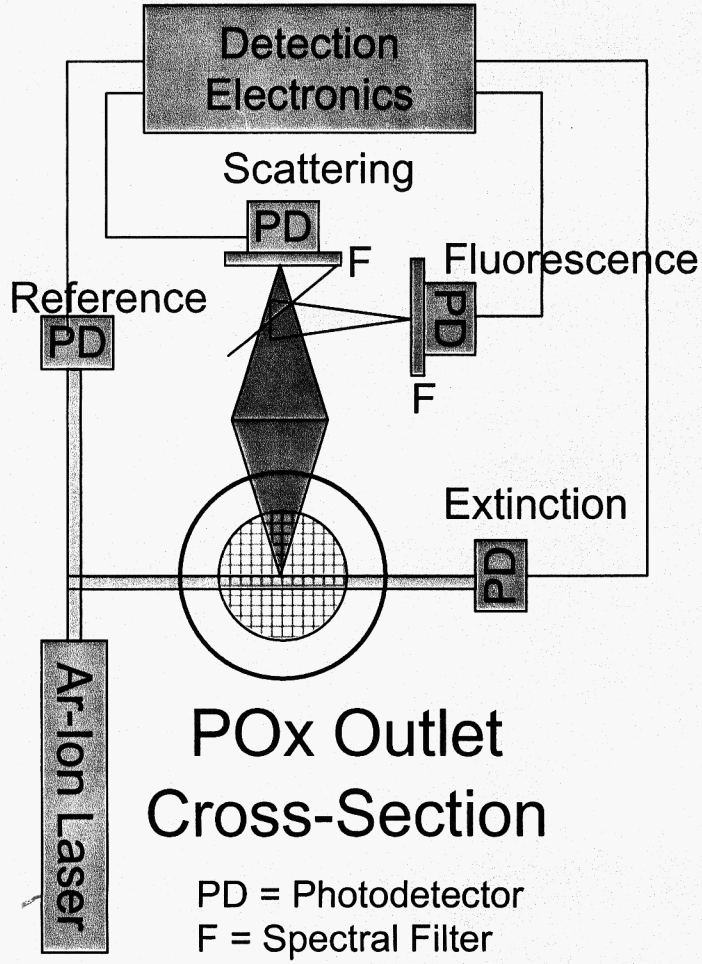
O/C = 0.85 | O/C = 0.76 | O/C = 0.70 | O/C = 1.0

Carbon Formation Observed

Once on-set of carbon formation is initiated,
increase in oxygen increases outlet monolith temperature;
yet carbon formation remains

S/C = 1.0, Residence time = 15 msec

Measurement of Incipient Carbon Formation

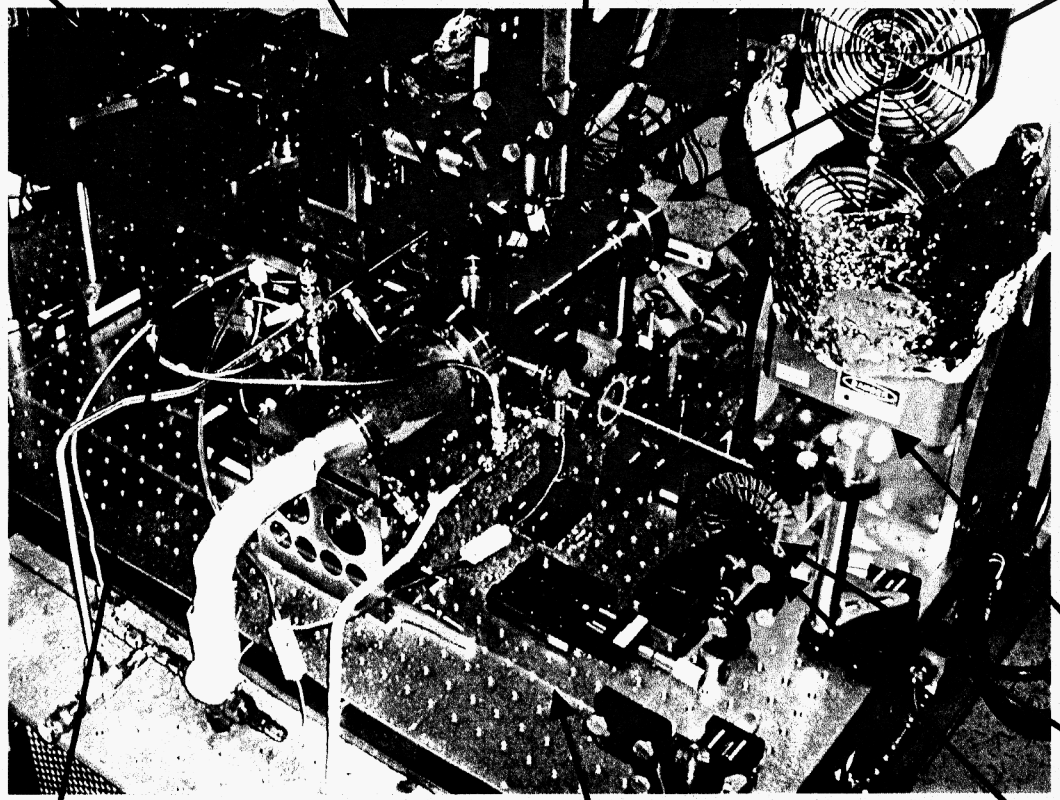


POx Outlet Cross-Section

PD = Photodetector
F = Spectral Filter

- Simplified schematic of a laser scattering-extinction system (not all components shown)
- Laser scattering-extinction system provides a real-time measurement of carbon particles or soot formation
- Spectral Detection allows for fluorescence detection of PAHs – considered precursors to soot
- Flange with purged windows to allow optical access to outlet of POx
- Probe sampling coupled to online mass spec allows detection of higher AMU compounds (< 200 amu)

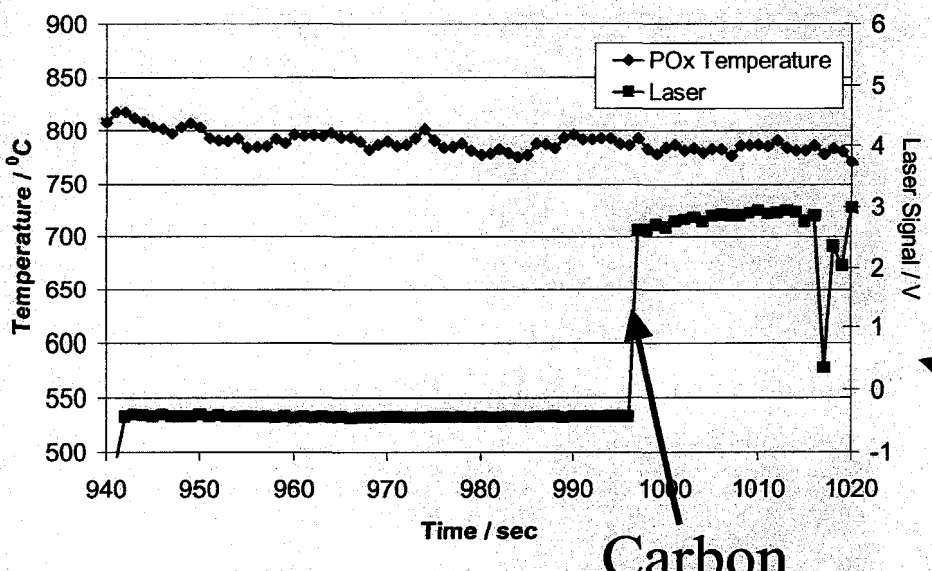
Carbon Formation Laser Optics



- Laser extinction measurements monitor on-set of carbon
- Laser scattering quantifies carbon formation
- Fluorescence indicates PAHCs

Carbon Formation Laser Optics

- Measurement of carbon on-set
- Currently working on absorbance for direct measure of carbon quantity
- Incorporating fluorescence measurements of carbon precursors

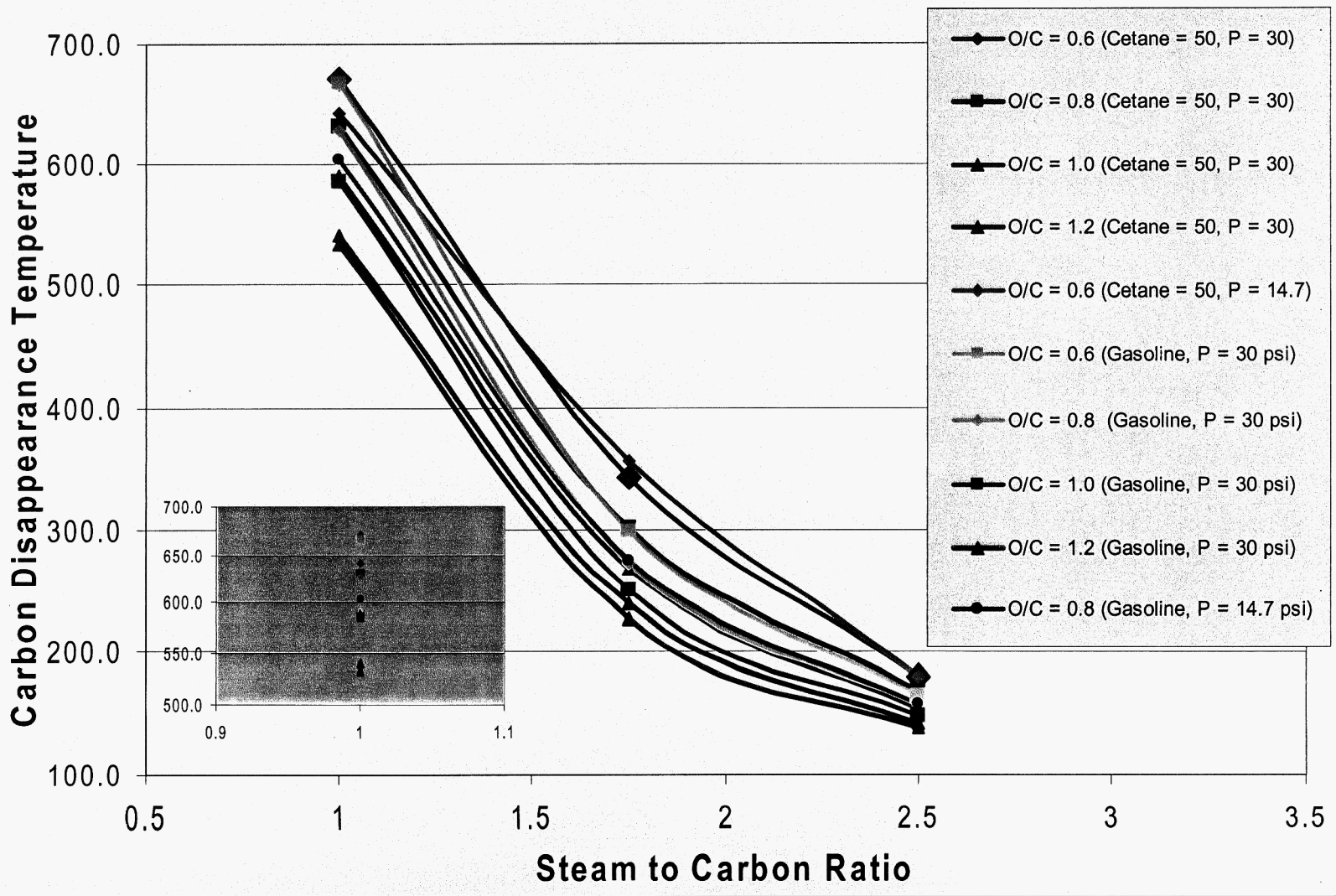


Carbon Formation

- Real time measurement
  - Visual ~ 10% absorbance
  - Laser < 2% absorbance

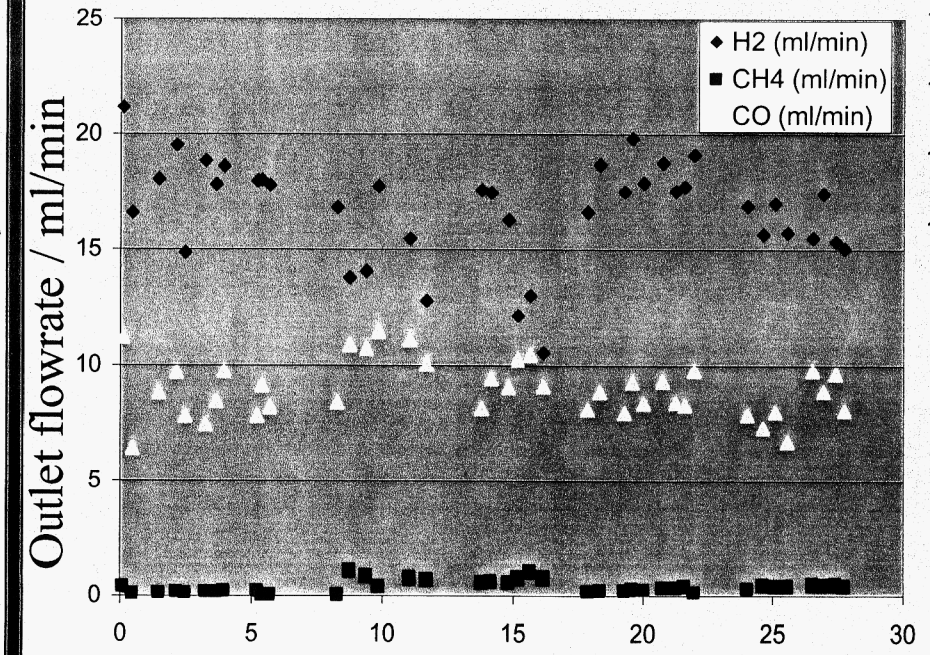
Turned steam off to show carbon absorbance of laser

Modeling of Carbon Formation Disappearance for Different Fuel Compositions

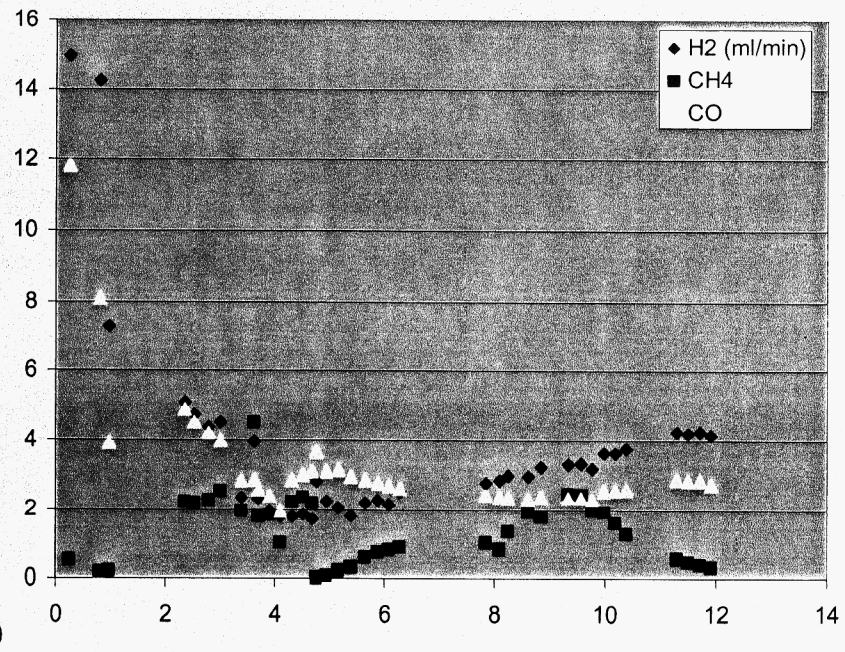


Partial oxidation of Iso-octane over Ni/Al_2O_3
(750°C, O/C = 0.76, H_2O/C = 1.15)

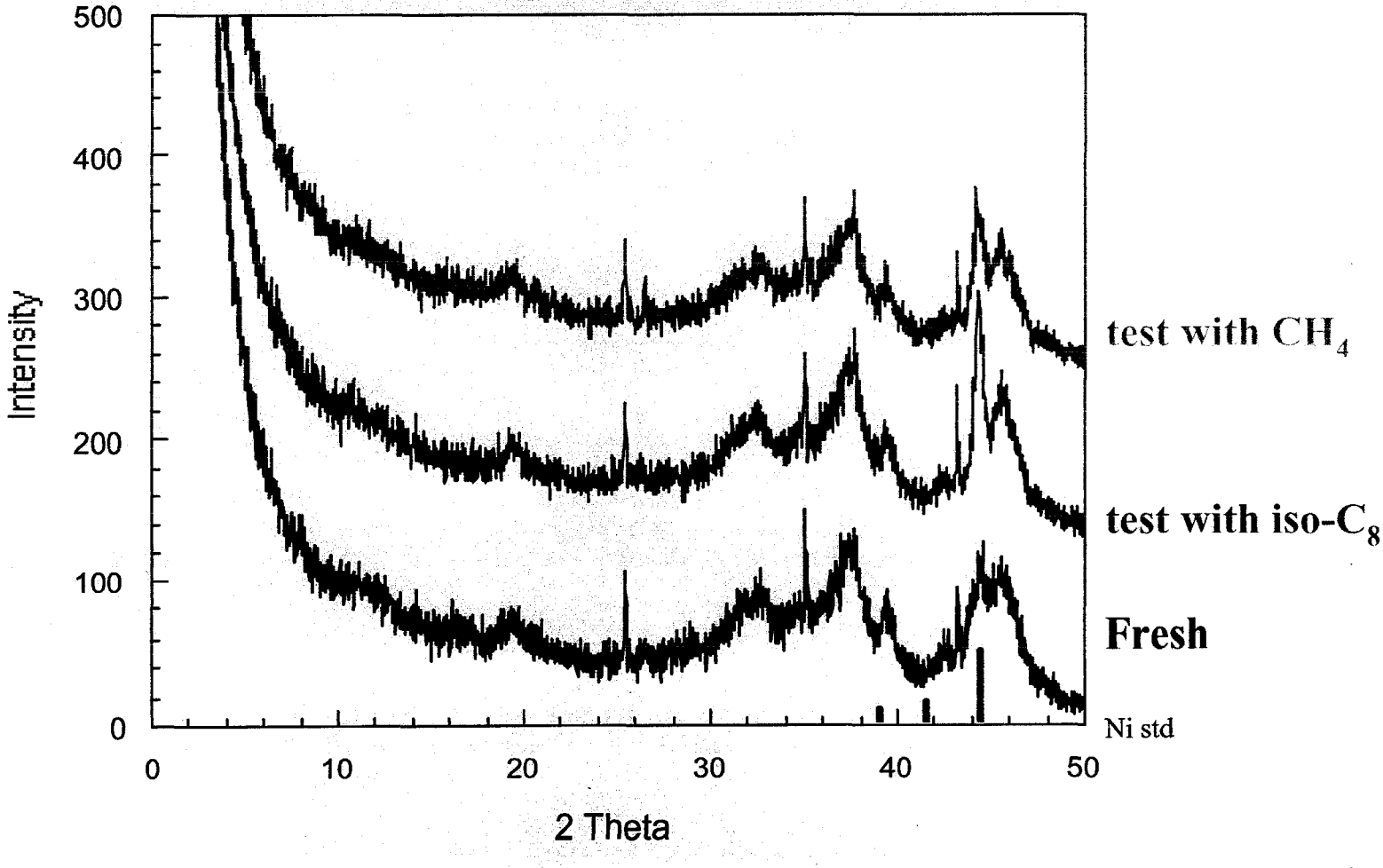
iso-Octane



100 ppm Sulfur in iso-Octane

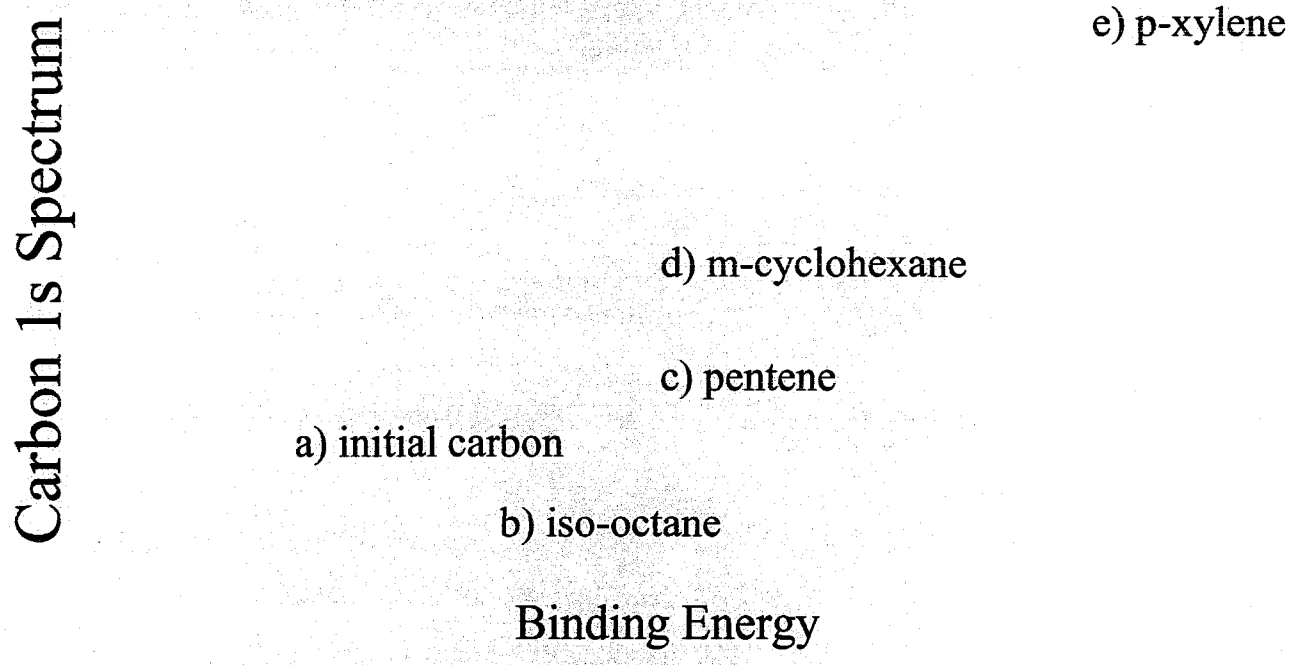


X-ray diffraction: 5% Ni/Al_2O_3



XPS Post Characterization of Catalysts

Carbon 1s Spectrum for Ni/Al_2O_3 Catalysts



- Elemental Analysis / Chemical Shift
  - large amounts of carbon formation:
    - p-xylene >> methylcyclohexane > 1-pentene >> iso-octane
  - NiC (nickel carbide) was formed with p-xylene
  - Carbon shifting to lower binding energies with increasing quantity
    - different carbon species?

Low noble metal loaded ATR fuel processor

- Low noble metal loaded fuel processor
  - demonstrated low noble metal loaded ATR
    - low loaded Pt / Al_2O_3 washcoat / 400 cpsi monolith
    - 1 g total Pt catalyst loading
  - non-noble metal steam reforming unit
    - Ni/Al_2O_3 or promoted Ni/Al_2O_3

- Operation to > 60 kW LHV fuel in (with iso-octane)
  - about 30 kW LHV with aromatic compounds for similar O_2 conversion in POx section
  - Operation with simulated gasoline fuel components (no sulfur)

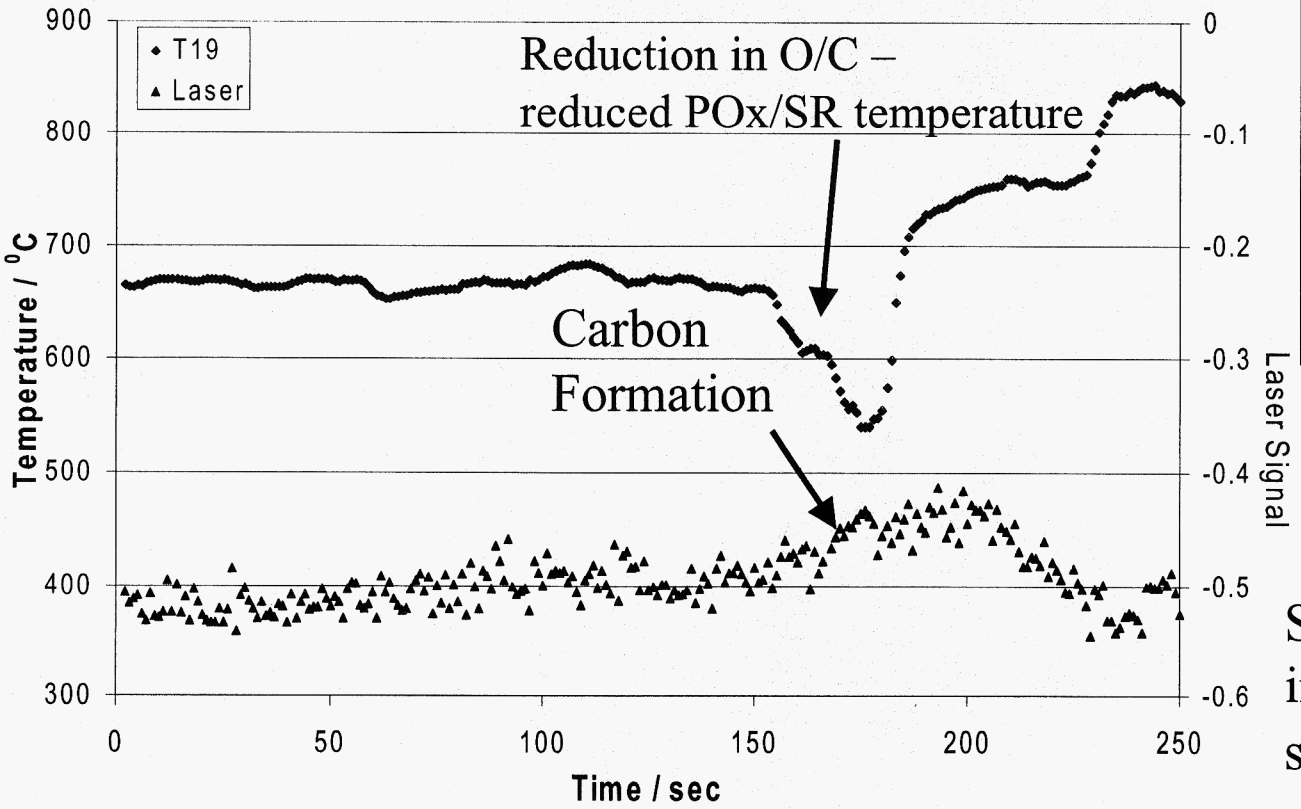
- Scales to ~ 2 g Pt for > 50 kW electric equivalent ($20 / g Pt)
  - noble metal loading dependent upon fuel

CO Chemisorption Results

Sample #	CO Chemisorption	Dispersion	Crystallite Diameter	Metal Surface Area	Metal Surface Area
(Description)	(ccSTP/g at 55 Torr)	(%)	(nm)	(m2/g catalyst)	(m2/ g metal)
1. (Fresh .5% Rh/Al_2O_3)	0.4278	39.31	3.4	0.718	143.6
2. (Fresh .5% Rh/Al_2O_3 with CH_4)	0.1502	13.8	9.6	0.254	50.8
3. (Fresh .5% Rh/Al_2O_3 with iso-octane)	Negligible	V. Low	V Large	Negligible	Negligible
4. (Fresh 5% Ni/Al_2O_3)	0.97	5.08	24.1	1.4	28
5. (5% Ni/Al_2O_3 with iso-octane)	0.819	4.29	28.5	1.18	23.6
6. (5% Ni/Al_2O_3 with CH_4)	0.164	0.86	143	0.235	4.7

Carbon Formation Laser Optics

Measurement of carbon on-set



Fuel: Naptha
S/C = 0.5
O/C = varied

Carbon Disappearance Modeling predicted:
~ 600 °C for S/C = 1.0

Signal/noise will improve with scattering measurements

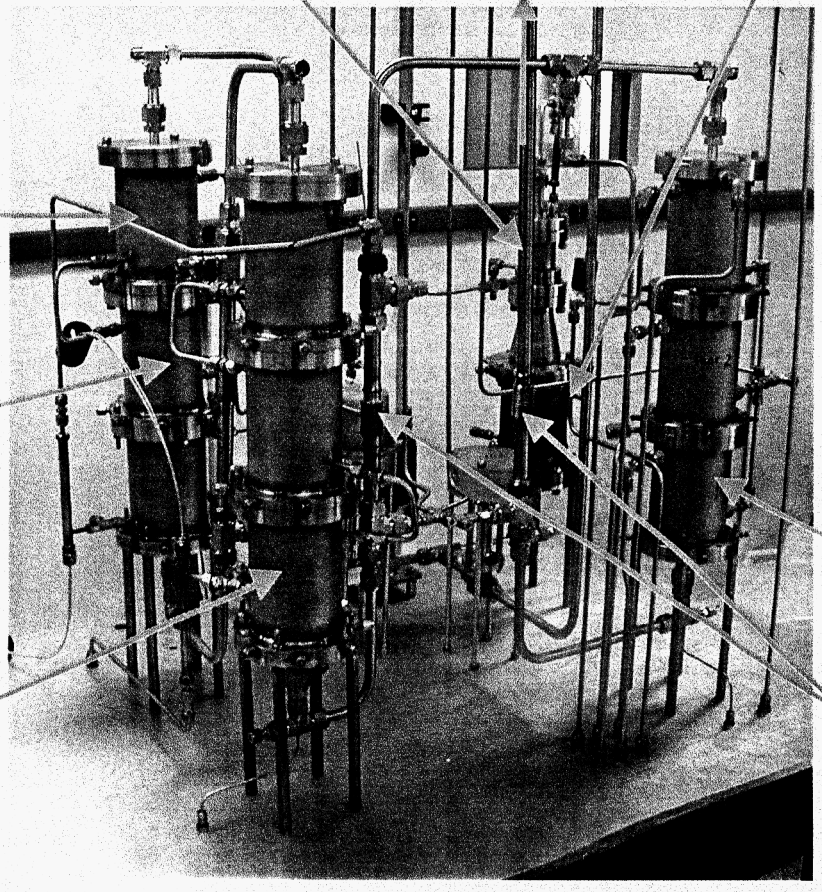
Noble metal oxidation (monolith)
Ni SR catalyst (pellets)
Laser signal due to carbon 'suppressed' due to metal mesh (holding Ni Pellets)

Estimate of Anode Catalyst Poisoning

MEA Assumptions		
Catalyst Surface area	120	m2/g Pt
Anode Loading	0.1	mg/cm2
MEA Pt Surface area	0.012	m2 Pt /cm2 membrane
MEA Pt Surface area	120	cm2 Pt /cm2 membrane
EC Charge for Pt surface	210	microCoulombs/cm2 Pt
Pt Surface sites	1.31E+15	Pt surface sites / cm2 Pt s.a.
MEA Pt Surface sites	1.57E+17	# Pt sites / cm2 membrane
Pt utilization	50	%
Available surface sites	7.87E+16	# Pt sites / cm2 membrane
Stack Assumptions:		
Anode Stoich	1.2	
Current Density	0.5	Amp/cm2
Hydrogen flowrate	1.56055E+18	molecules H2/sec-cm2 MEA
Hydrogen flowrate	0.003484017	SLPM/cm2 MEA
Hydrogen Concentration	40	%
Total Molecular Flow	3.90E+18	molecules/sec - cm2 MEA
Contaminant Flowrate	3.90E+10	molecules/sec - cm2 MEA
Contaminant sticking coefficient	0.1	
Time for saturation	2.02E+07	sec
Time for saturation	**5,600.0**	**hr**
Contaminant Conc.	**0.01**	**ppm**

- System durability
  - 5000 hrs
- Impurity specifications
  - < 1 ppm NH_3
  - < 0.1 ppm H_2S
- Estimate by calculation
  - membrane sites
  - catalyst sites
- Potential 'irreversible' contaminants need to be < 0.01 ppm (< 10 ppb)

Fuel Processing Section of Durability Test Fixture



Modular System Design:

heated/cooled reactor shells
variable reactor temperatures
change reactor configuration
temperatures, catalysts

Various Impurity Concentrations

Steam reforming conditions:

S/C = 1.0, O/C = 0.7, T = 700 ^{0}C

Equilibrium calculations

HCN – 0.4 ppm

NH_3 – 89 ppm

C2H2 - 0.03 ppb

C2H4 – 12 ppb

HCN, NH_3 - None detected to low levels
what happens to bound Nitrogen
(Naptha < 0.15 %N)

Experimentally Measured

HCN – ND

NH_3 – ND

C2H2 – (up to) 600 ppm

C2H4 – 250 ppm

Technical Progress Summary/Findings

- Homogeneous oxidation
  - easier with 'real' fuels than pure components \
- Catalytic oxidation
  - aromatics slow and inhibit overall reaction rate
- Carbon Formation
  - Hysteresis observed after on-set of carbon formation
  - Greater carbon formation with aromatics
- Diesel Fuel Components (Dodecane)
  - Lower conversion / higher residence time required for O2 conversion
- Laser & visual monitoring of carbon formation

Summary

Catalyst Effects and Characterization

- **Pt/Al_2O_3, Rh/Al_2O_3 and unpromoted / promoted Ni/Al_2O_3 catalysts**
- **Unwashcoated noble metal catalyst show low activity**
- **Decreased surface area after testing**
- **Less carbon formation with promoted Nickel steam reforming catalyst**

Plans and Future work

- **Lifetime tests with candidate fuels / catalysts**
  - **monitor catalytic activity with operational time with fuel constituents**
  - **evaluate the reforming kinetics as f(catalyst, fuel)**
- **Fuel effect comparison between catalytic and homogeneous partial oxidation**

Acknowledgments

- **This work was funded by the Department of Energy, Office of Advanced Automotive Technologies**
  - **Pete Devlin** **Program Manager: Fuels for Fuel Cells**
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  - **Mark Paffet (CST-18, LANL)**